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PATENT SPECIFICATION

NO DRAWINGS

856,327



Date of Application and filing Complete Specification Sept. 30, 1957.

No. 30541/57.

Application made in United States of America on Oct. 2, 1956.

Complete Specification Published Dec. 14, 1960.

Index at acceptance:—Classes 2 (6), P1A, P1C(4B:5:6B:13B:13C:17:20B:20C), P1(D1B:F2:S3), P4A, P4C(4B:5:6B:13B:13C:17:20:20C), P4D(1A:3B1), P4F2, P4(K10:S3), P7A, P7C(4B:5:6B:13B:13C:17:20B:20C), P7D(2A1:3), P7(F2:K8), P8A, P8C(4B:5:6B:13B:13C:17:20B:20C), P8D(1B:3A:4), P8F2, P8K(7:10), P8S3, P10A, P10C(4B:5:6B:13B:13C:17:20B:20C), P10D(1A:2A), P10F2, P10K(4:8:10), P10S3, P11A, P11C(4B:5:6B:13B:13C:17:20B:20C), P11D2A; 53, BS4F; and 87(2), C7D.

International Classification:—B29b. C08f. H01m.

COMPLETE SPECIFICATION

Membrane Materials and Process for Producing the same

We, POLYTECHNIC INSTITUTE OF BROOKLYN, a chartered corporation of the State of New York, United States of America, of 99, Livingston Street, Brooklyn 1, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel compositions of matter. More particularly, the invention contemplates the provision of new and improved membrane materials or membranaceous compositions of controlled microporosity useful as electrode separators within batteries and for similar applications.

The principal requisites of a battery separator of the general class described as used in conventional type lead acid storage batteries or any of the alkaline electrolyte type batteries, are maximum chemical stability and a low electrical resistance for maximum diffusion of electrolyte in order to minimize the internal resistance of the over-all assembly. Other necessary properties include, sufficient mechanical strength to withstand handling during assembly of the battery, shape or dimensional stability when wet with electrolyte, and sufficient density to resist piercing of the separator and possible short circuiting of the cell under action of metallic growths.

Heretofore, separators for alkaline batteries have been formed of cellulosic or modified cellulosic type materials. For example, United States Patent No. 2,317,711 as issued on April 27, 1943, to Henri G. Andre, and entitled "Accumulator", discloses a secondary battery in which the positive active plate is formed

of a substance such as silver oxide, silver peroxide, or combinations thereof, whereas the negative plate is formed of zinc, and separation of the respective electrodes is effected by wrapping the positive plate within a membrane of regenerated cellulose. While the use of cellulose or modified cellulosic materials as separators for alkaline electrolyte batteries is satisfactory initially, it has been found in general that such substances tend to breakdown upon extended exposure to standard alkaline electrolytes, and, in the silver-zinc cell, due to the oxidizing nature of the positive electrode. As a result, the separator loses its initial insulating properties and is pierced readily by the growth or "treeing" of the metallic components, thereby severely limiting the life cycle of a secondary battery of this type.

The use of microporous polymeric films as battery separators has also been practised heretofore. For example, the manufacture of such films is disclosed in United States Patents Nos. 2,542,527 issued on February 20, 1951, to Honey *et al* and entitled, "Process of Producing Microporous Material", and 2,676,929 issued on April 27, 1954, to Joseph C. Duddy and entitled, "Stock Material for Microporous Articles and Methods of Making the Same from Starch and Polyethylene". In these patented processes, polymeric materials such as polyvinyl chloride or polyethylene are admixed with finely-ground starch particles and the mixture cast into sheets. Thereafter, by successive treatments and washing in both acid and alkaline media the starch particles are hydrolyzed and rendered soluble, leaving in their place voids of the approximate size of the original particles. While this

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type of microporous material has found commercial application in the lead acid battery, the nickel-cadmium battery, and the mercury-zinc cell, among others, its principal disadvantages are the relatively high cost of manufacture, the difficulty experienced during manufacture in maintaining close control of the pore size in the finished product, and the inability of the process to achieve pores of the order of 1000—2000 Å which are desirable in certain battery applications as, for example, in the silver peroxide-zinc alkaline cell.

Various techniques for incorporating ion exchange resins into membranaceous sheet form have also been proposed heretofore. These are described in United States Patents Nos. 2,614,976 of October 21, 1952, to Patnode *et al*, entitled, "Electrode for Determining Cationic Activity"; 2,681,319 of June 15, 1954, to George W. Bodamer for "Permeable Films of Anion-Exchange Resins"; and 2,681,320 of June 15, 1954, to George W. Bodamer for "Permeable Films of Cation-Exchange Resins". The techniques employed in accordance with these patents involve either molding of the ion exchange resin and a binder using elevated temperatures and pressures, or sheeting-out of an inert plastic binder on a heated roller mill with mixing of the ion exchange resin particles being effected under continuous milling until the mixture is uniform. In general, the disadvantages of the membranes formed by these processes are their relatively high electrical resistance and the relatively low resin to binder ratio which can be obtained.

It is the principal object of the present invention to provide relatively low cost separator materials of enhanced physical and operational characteristics, that is, materials of low electrical resistance and controlled pore size and pore size distribution which will permit free diffusion of electrolyte while mechanically screening metallic ions from the active material, thereby preventing their passage from a plate of one polarity to the plate of opposite polarity; materials which are formed of inert components such that the separator membranes are highly resistant to strong acid, strong base, and potent oxidizing environments; and materials which further possess such mechanical and physical properties as to greatly facilitate the assembling of battery structures.

The separator of our invention comprises a membranaceous composition characterised by a microporous film-like polymeric matrix formed of a material selected from the group consisting of polyvinyl chloride, polyvinyl butyral, and copolymers of vinyl chloride with monomers selected from the group consisting of vinyl acetate, vinylidene chloride and acrylonitrile, the matrix having a finely-divided solid hydrophilic polymeric material which is

characterized by the ability to swell in water and aqueous solutions uniformly dispersed therethrough and firmly held therein, the polymeric matrix material and hydrophilic polymeric material being present in proportions within the range of from 1 to 4 parts by weight of hydrophilic material to each part by weight of matrix material.

Suitably a substantially inert synthetic fibrous reinforcing material is contained within the microporous film-like polymeric matrix.

The hydrophilic polymeric material may consist of a non-ion-selective substance selected from the group consisting of polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylamide and water soluble natural gums or of an ion-selective cross-linked polymeric substance.

When used as an electrode separator in batteries utilizing acid and alkaline electrolytes the matrix may consist of a copolymer of polyvinyl chloride and acrylonitrile having uniformly dispersed therethrough finely divided solid particles of polyvinyl alcohol. When used as an electrode separator in batteries of the silver-zinc alkaline electrolyte type the finely divided solid particles may be of a cross-linked copolymer of methacrylic acid and divinyl benzene. In the latter case the polymeric matrix and the cross-linked copolymer may be present in respective proportions equal to approximately 300 parts of cross linked copolymer per 100 parts of matrix.

When used as an electrode separator in batteries of the nickel-cadmium type the dispersion in the matrix may consist of a weak base polyamine type ion-exchange resin.

In batteries of the lead-acid type the dispersion may be a strong acid type ion exchange resin, a polystyrene sulfonic acid and ion-exchange resin, a polystyrene sulfonic acid ion-exchange resin, a polystyrene phosphonic acid ion-exchange resin or a strong base type ion-exchange resin.

If a more flexible film is necessary or desirable, conventional vinyl plasticizers of the non-ester type as, for example, high molecular weight aromatic hydrocarbons, may be added in small proportions.

When the composition is intended for use as a dialyzing membrane, the polymeric matrix material and hydrophilic polymeric material may be present in proportions equal to less than 1 part of hydrophilic material to each part of matrix material.

In producing the microporous membranaceous composition of the film-forming polymeric matrix material with the monomers is admixed within a solvent system of at least limited solubility with respect to the matrix material, finely-divided solid particles of the hydrophilic polymeric material are incorporated within the mixture of solvent and matrix material to form a uniform suspension of the hydrophilic polymeric material within

the matrix material, the mixture of polymeric materials is subjected to a sheeting operation and the sheeted mixture subjected to a leaching operation for a period of time sufficient to effect elimination of the solvent and the introduction of micropores into the matrix material while avoiding the removal of any appreciable portion of the hydrophilic polymeric material. The polymer matrix material should be soluble to the extent of at least five percent within the solvent system which in turn should be at least slightly soluble within the leaching medium, the leaching operation being controlled for control of pore size and pore size distribution within the membranaceous composition.

A suitable solvent for the matrix material can be selected from the group consisting of methyl ethyl ketone, methyl isobutyl ketone, acetone, cyclopentanone, dimethyl formamide, glycolmonoethylether, and diethylene glycolmonoethylether, and the controlled elimination of the solvent from the cast-sheet effected by preliminary partial drying at a temperature within the range of 45–95° C., followed by the leaching of the cast-sheet.

It is believed that the invention may be best understood by reference to the following specific examples of typical preparations of separator membranes and applications of the same.

EXAMPLE I

A matrix material consisting of a 50–50 copolymer of polyvinyl chloride and acrylonitrile (Bakelite NYGL resin), in amount of four and one-half parts, was dissolved in 25.5 parts of dimethyl formamide. To this solution there were added 13.5 parts of finely-ground (–200 mesh) polyvinyl alcohol (Elvanol 51–05), and 56.5 parts of dimethyl formamide. The resulting mixture was stirred to obtain a homogeneous slurry. After the mixture was permitted to stand for at least fifteen (15) minutes to deaerate (but not longer than 8 hours because of an increasing viscosity), the membrane was formed by coating a flat surface with a uniform thickness (6 to 20 thousandths of an inch) of the slurry, and, thereafter, the solvent was removed by immersing the coated plate into a running water bath maintained at approximately room temperature. The solvent leaching was continued for a minimum of ten (10) minutes, after which the film was removed and dried.

The foregoing membrane, at 8 mils thickness, has an electrical resistance of 10–20 milliohms per square inch when saturated with thirty-one percent (31%) potassium hydroxide. The average effective pore diameter present, as calculated from liquid permeability data, is of the order of 2000 Å. It is ideally suited for use in batteries for purposes of isolating adjacent positive and negative plates. For example, when the material was wrapped around a silver peroxide electrode in order to

isolate it from a zinc electrode, the life of this alkaline system on cycling was extended by at least a factor of two hundred percent (200%) when compared to similar electrode components wrapped with commercial cellulosic separator material.

EXAMPLE II

A matrix material consisting of a 50–50 copolymer of polyvinyl chloride and acrylonitrile, in amount of four and one-half parts, was dissolved in 25.5 parts of dimethyl formamide. To this solution there were added 13.5 parts of finely-ground (–100 mesh) polyvinyl alcohol, and 56.5 parts of dimethyl formamide, to obtain a uniform or homogeneous suspension. An open weave nylon marquisette of approximately 5 mils thickness was passed through the slurry and then through a pair of stainless steel stationary rollers set a fixed distance apart (7 mils). The solvent was then removed by immersing the doctored film in a water bath for ten (10) minutes with the formation of a flexible reinforced membrane. The separator material was finished by drying at a temperature below 60° C. to remove the water.

EXAMPLE III

The procedure described in Example I was repeated with polyvinyl butyral (Celanese PK–5 or Bakelite XYHL) being employed as the film forming material. This was accomplished by dissolving 8 parts of the polyvinyl butyral in 92 parts of ethylene glycol monoethyl ether (Cellosolve), and thereafter adding 24 parts of 200 mesh polyvinyl alcohol (Elvanol 51–05) with strong stirring. Thereafter, 32 parts of Cellosolve were used to thin the resulting slurry to a proper consistency for casting. The formation of the membrane was effected in exactly the same manner as previously described in Example I.

EXAMPLE IV

One part of a polymer matrix material consisting of a 50–50 copolymer of polyvinyl chloride and acrylonitrile (Bakelite NYGL) was dissolved in six parts of dimethyl formamide. To this mixture there was added one part of water soluble Karaya gum (hydrophil 1150-Morningstar-Nicol) of –200 mesh, and the mixture was stirred to a uniform slurry. The film was cast as described in Example I, and the solvent removed to the extent of porosity desired in the final product, either by complete evaporation, or by partial evaporation followed by coagulation in a non-aqueous solvent such as methanol. A flexible, strong film was obtained which swells in electrolyte to impart low electrical resistance characteristics to the material.

EXAMPLE V

Sixty-four and one-half (64½) parts of Bakelite resin NYGL, previously dissolved in di-

methyl formamide to form a fifteen percent (15%) solution, and 19.4 parts of a weak base polyamine resin (Rohm & Haas XE-114; -200 mesh), which was previously soaked in 61.4 parts of dimethyl formamide for a period of at least four hours, were mixed together to obtain a uniform or homogeneous slurry. Soaking of the resin in dimethyl formamide was practised to swell the same prior to admixture with the binder, thereby insuring a relatively constant slurry viscosity for long periods of time.

The foregoing slurry was cast by extruding a 10 mil quantity onto a glass plate. Following the casting, the resulting membrane was dried at 40-45° C. until the surface of the film became dull (7-10 minutes). The membrane was then placed in a running water coagulating bath for at least ten minutes.

The membrane was tested as a separator for the silver peroxide-zinc alkaline cell and gave at least a two hundred percent (200%) improvement in cycle life as compared to the performance of a cellulosic membrane.

EXAMPLE VI

The procedure described in Example V was modified by use of a carboxylic acid-type resin (Rohm & Haas IRC-50). The slurry used in forming the casting was made up of 63.0 parts of the fifteen percent (15%) solution of Bakelite NYGL resin in dimethyl formamide admixed with 24.0 parts of the carboxylic acid resin (-200 mesh). Prior to use, the ion exchange resin was mixed with 80.0 parts of dimethyl formamide was allowed to soak for at least four hours.

The slurry was cast on a flat plate (10 mils) and then dried at 90-100° C. for a period of three to five minutes. This was followed by a coagulation and solvent leaching in running water.

The foregoing membrane was also tested as a separator for the silver peroxide-zinc alkaline cell and demonstrated a three hundred percent (300%) improvement in cycle life as compared to the equivalent testing of a cellulosic membrane.

The foregoing procedure was repeated with strong acid-type resins (National Aluminate Corp.-phosphonic resin: Dow Chemical Company-Dowex 50) and equivalent results were obtained upon testing of the resulting membranes.

The foregoing procedure was also repeated with a strong base-type ion-exchange resin (Dowex 1) and equivalent results obtained with the resulting membrane.

EXAMPLE VII

Seven and one-half (7½) parts of a polymeric matrix material consisting of polyvinyl butyral (Celanese PX-2, PX-5 or Bakelite XYHL) were dissolved in 70 parts of ethylene glycol monoethyl ether (Cellosolve). To this

solution there were added 22.5 parts of a finely-ground (-200 mesh) polystyrene sulfonic acid resin (Dowex 50), and 0.5 part of a vinyl plasticizer (Mobilsol C or Sovaloid C). The resulting mixture was stirred to obtain a uniform suspension, and the slurry was deaerated and cast into sheet form. The solvent was partially evaporated by subjecting the film to drying conditions in an oven maintained at 90-100° C. for a period of two to five minutes. The solvent remaining following evaporation drying was removed by immersing the wet film in a coagulating bath of running water. The resulting membrane exhibited excellent properties for use as a battery separator.

The foregoing procedure was repeated with the following resins and a satisfactory membrane was obtained in each instance:—

- 1) a weak base resin (Rohm & Haas XE-114);
- 2) a strong base resin (Dowex 1); and
- 3) a weak acid-type ion exchange resin of the cross-linked polyacrylic acid-type (IRC-50). (The words "Cellosolve", "Mobilsol", "Sovaloid", "Celanese" and "Bakelite" are Registered Trade Marks).

EXAMPLE VIII

Twenty-four (24) parts of a finely-divided (-200 mesh) carboxylic acid resin (Rohm & Haas IRC-50), which had been soaked in eighty (80) parts of dimethyl formamide for at least four hours, were stirred into sixty-three (63) parts of a fifteen percent (15%) solution of Bakelite NYGL resin dissolved in dimethyl formamide. The mixture was stirred until a smooth, homogeneous slurry was obtained. An open weave nylon marquisette was passed through the slurry and then through a pair of stainless steel rollers spaced a fixed distance apart. The solvent was removed by immersing the doctored reinforced film in a water bath to form a flexible-reinforced membrane of excellent separator characteristics.

WHAT WE CLAIM IS:—

1. A membranaceous composition characterized by a microporous film-like polymeric matrix formed of a material selected from the group consisting of polyvinyl chloride, polyvinyl butyral, and copolymers of vinyl chloride with monomers selected from the group consisting of vinyl acetate, vinylidene chloride and acrylonitrile; said matrix having a finely-divided solid hydrophilic polymeric material, which is characterized by the ability to swell in water and aqueous solutions, uniformly dispersed therethrough and firmly held therein, the polymeric matrix material and hydrophilic polymeric material being present in proportions within the range of from 1 to 4 parts by weight hydrophilic material to each part by weight matrix material.
2. The membranaceous composition as

claimed in Claim 1, and further characterized by a substantially inert synthetic fibrous reinforcing material contained within said microporous film-like polymeric matrix.

5 3. The membranaceous composition as claimed in Claim 1, wherein said hydrophilic polymeric material consists of a non-ion-selective substance selected from the group consisting of polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylamide and water-soluble natural gums.

10 4. The membranaceous composition as claimed in Claim 1, wherein said hydrophilic polymeric material consists of an ion-selective, cross-linked polymeric substance.

15 5. A membranaceous composition as claimed in Claims 1 and 2, characterized by low electrical operating resistance and intended for use as an electrode separator within batteries of the type utilizing acid and alkaline electrolytes, wherein said microporous film-like polymeric matrix consists of a copolymer of polyvinyl chloride and acrylonitrile having uniformly dispersed therethrough and firmly held therein, finely-divided solid particles of polyvinyl alcohol.

20 6. A membranaceous composition as claimed in Claims 1 and 2, characterized by a low electrical operating resistance and intended for use as an electrode separator within batteries of the silver-zinc alkaline electrolyte type, wherein said microporous film-like polymeric matrix consists of a copolymer of polyvinyl chloride and acrylonitrile having uniformly dispersed therethrough and firmly held therein, finely-divided solid particles of a cross-linked copolymer of methacrylic acid and divinyl benzene.

30 7. The membranaceous battery separator as claimed in Claim 6, wherein said polymeric matrix and cross-linked copolymer are present in respective proportions equal to approximately 300 parts of cross-linked copolymer per 100 parts of matrix.

45 8. A membranaceous composition as claimed in Claims 1 and 2, characterized by low electrical operating resistance and intended for use as an electrode separator within batteries of the nickel-cadmium type, wherein said microporous film-like polymeric matrix consists of a copolymer of polyvinyl chloride and acrylonitrile having uniformly dispersed therethrough and firmly held therein, a weak base polyamine type ion-exchange resin.

55 9. A membranaceous composition as claimed in Claims 1 and 2, characterized by low electrical operating resistance and intended for use as an electrode separator within batteries of the lead-acid type, wherein said microporous film-like polymeric matrix consists of a copolymer of polyvinyl chloride and acrylonitrile having uniformly dispersed therethrough and firmly held therein, a strong acid type ion-exchange resin.

65 10. A membranaceous composition as

claimed in Claims 1 and 2, characterized by low electrical operating resistance and intended for use as an electrode separator within batteries of the lead-acid type, wherein said microporous film-like polymeric matrix consists of a copolymer of polyvinyl chloride and acrylonitrile having uniformly dispersed therethrough and firmly held therein, a polystyrene sulfonic acid ion-exchange resin.

11. A membranaceous composition as claimed in Claims 1 and 2, characterized by low electrical operating resistance and intended for use as an electrode separator within batteries of the lead-acid type, wherein said microporous film-like polymeric matrix consists of a copolymer of polyvinyl chloride and acrylonitrile having uniformly dispersed therethrough and firmly held therein, a polystyrene phosphonic acid ion-exchange resin.

12. A membranaceous composition as claimed in Claims 1 and 2, characterized by low electrical operating resistance and intended for use as an electrode separator within batteries of the lead-acid type, wherein said microporous film-like polymeric matrix consists of a copolymer of polyvinyl chloride and acrylonitrile having uniformly dispersed therethrough and firmly held therein, a strong base type ion-exchange resin.

13. The membranaceous composition as claimed in any of the preceding claims, further characterized by the presence within said matrix of a small proportion of a flexibilizing agent in the form of a high molecular weight aromatic hydro-carbon vinyl plasticizer.

14. The membranaceous composition as claimed in Claim 1 and intended for use as a dialyzing membrane, wherein the polymeric matrix material and hydrophilic polymeric material are present in respective proportions equal to less than 1 part hydrophilic material to each part matrix material.

15. A membranaceous composition as claimed in any of the preceding claims, produced by casting said polymeric matrix material and hydrophilic polymeric material into sheet-form while in admixture within a suitable solvent for the matrix material selected from the group consisting of methyl ethyl ketone, methyl isobutyl ketone, acetone, cyclopentanone, dimethyl formamide, glycolmonoethylether, and diethylene glycolmonoethylether, and thereafter effecting controlled elimination of said solvent from the cast-sheet by preliminary partial drying of the same at a temperature within the range 45—95° C., followed by leaching of the cast-sheet under conditions controlled to effect removal of the remaining solvent while avoiding removal of any appreciable portion of the hydrophilic polymeric material contained therein.

16. Process for the production of a microporous membranaceous composition characterized by admixing a film-forming polymeric matrix material selected from the group

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consisting of polyvinyl chloride, polyvinyl butyral, and copolymers of vinyl chloride with monomers selected from the group consisting of vinyl acetate, vinylidene chloride and acrylonitrile, within a solvent system of at least limited solubility with respect to said matrix material; incorporating finely-divided, solid particles of a hydrophilic polymeric material which is characterized by the ability to swell in water and aqueous solutions, within said mixture of solvent and matrix material to form a uniform suspension of the hydrophilic polymeric material within the matrix material; subjecting the mixture of polymeric materials to a sheeting operation; and subjecting the sheeted mixture to a leaching operation for a period of time sufficient to effect elimination of said solvent and the introduction of micro-

pores into said matrix material while avoiding the removal of any appreciable portion of the hydrophilic polymeric material suspended within said matrix material.

17. The process as claimed within Claim 16, wherein the polymeric matrix material is soluble to the extent of at least five percent (5%) within the solvent system, which is in turn at least slightly soluble within the leaching medium; the leaching operation being controlled for control of pore size and pore size distribution within the membranaceous composition.

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